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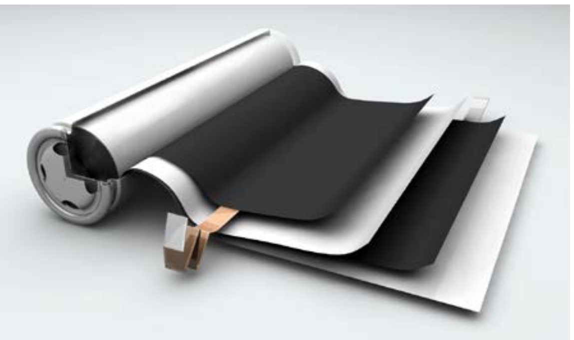
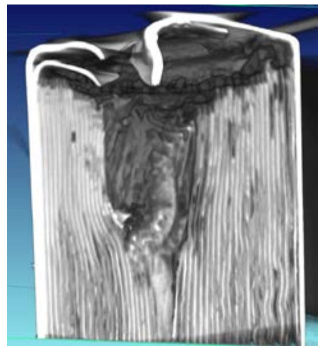

# Abuse Tolerance Improvements

**ES036**

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Sandia National Laboratories

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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# Overview

## Timeline

- Start Date: Oct. 2014
- End date: Oct. 2015
- Percent complete: >75%

## Budget

- FY15 Funding: $700K
  - Abuse Evaluation/Prototyping - $500K
  - Development of abuse-tolerant components - $200K
- FY14 Funding: $750K
- FY13 Funding: $1.0M

## Barriers

- Barriers addressed
  - Develop intrinsically abuse-tolerant lithium-ion cells and batteries
  - Issues related to cell safety are represent significant challenges to scaling up lithium-ion for transportation applications
  - Obtain access to latest promising materials from developers and sufficient quantities of materials to determine reproducibility of results

## Partners

- ANL, INL, NREL, ORNL, CU-Boulder
- XG Sciences, Physical Sciences Inc., Silatronix, Daikin

# Relevance and Objectives

***Developing inherently safe lithium-ion cell chemistries and systems***

1. **Evaluate Abuse Tolerance of High Energy Materials**
    - Understand the relative abuse response of higher energy materials in cells developed to meet the DOE EV goals
    - Materials of interest for lithium-ion batteries include LMR-NMC, high voltage spinel, and intermetallic anodes.
    - Characterization of abuse tolerance includes calorimetry, abuse testing, and analysis of gas decomposition products.
2. **Abuse Resilient Component Development**
    - Design and develop material components to mitigate the severity of thermal runaway in lithium-ion cells
3. **Evaluation of Abuse Resilient Electrolytes**
    - Build a series of >50 lithium-ion cells with various candidate and control electrolytes
    - Evaluate electrochemical performance and abuse tolerance of candidate electrolytes relative to the control
    - Make recommendations to VTO on candidate electrolytes that demonstrate good performance and improved abuse tolerance

# Milestones

**Demonstrate improved abuse-tolerant cells, and report to DOE and the battery community**

| Obj. | Milestone | Status |
|---|---|---|
| 1 | LMR-NMC: Abuse response of LMR-NMC materials | |
| 1 | HV cathodes: Abuse response of high voltage cathode materials | Q3 |
| 1 | Intermetallic anodes: Abuse response of Si- and other intermetallic anode materials from ABR competitive projects (FY13 project deliverables) | Q4 |
| 2 | SNL ABA: ABA Scale-up at MERF | |
| 2 | SNL ABA: Evaluation of MERF scaled ABA, confirm performance | |
| 2 | SNL ABA: Identification of new candidate ABAs | |
| 3 | Electrolyte Study: Performance and safety evaluation of advanced electrolytes (ABA, Phosphazene, organosilicon, HFE) | Q4 |

Milestone Complete

# Approach

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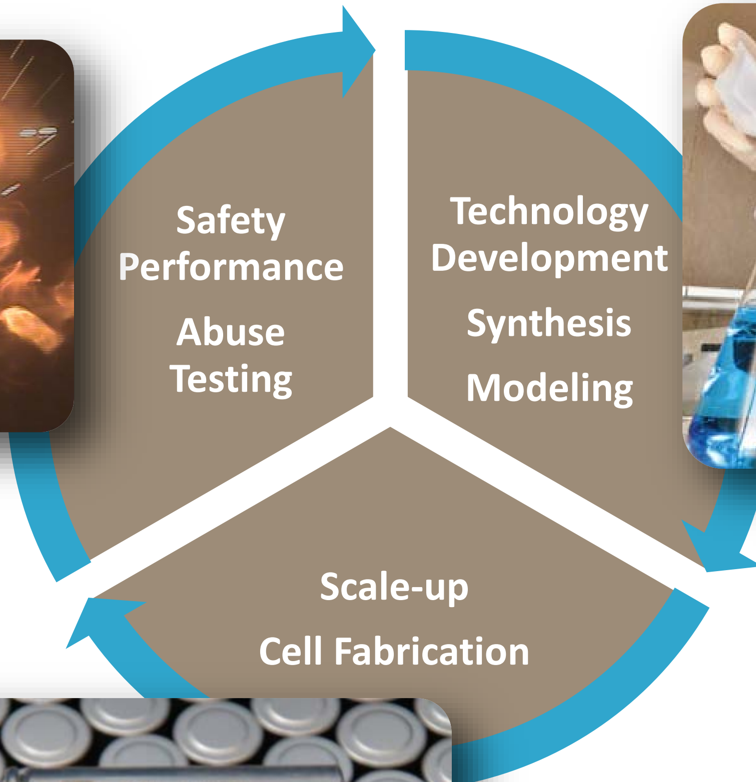


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# Technical Accomplishments/Progress/Results

## Abuse Tolerance of High Energy Materials:

- **LMR-NMC**
  - ARC measurements and abuse tolerance of LMR-NMC cells
- **Si-C anode characterization (XG Sciences):**
  - Separate anode ARC measurements of Si-C and graphite electrodes to quantify differences in anode runaway response

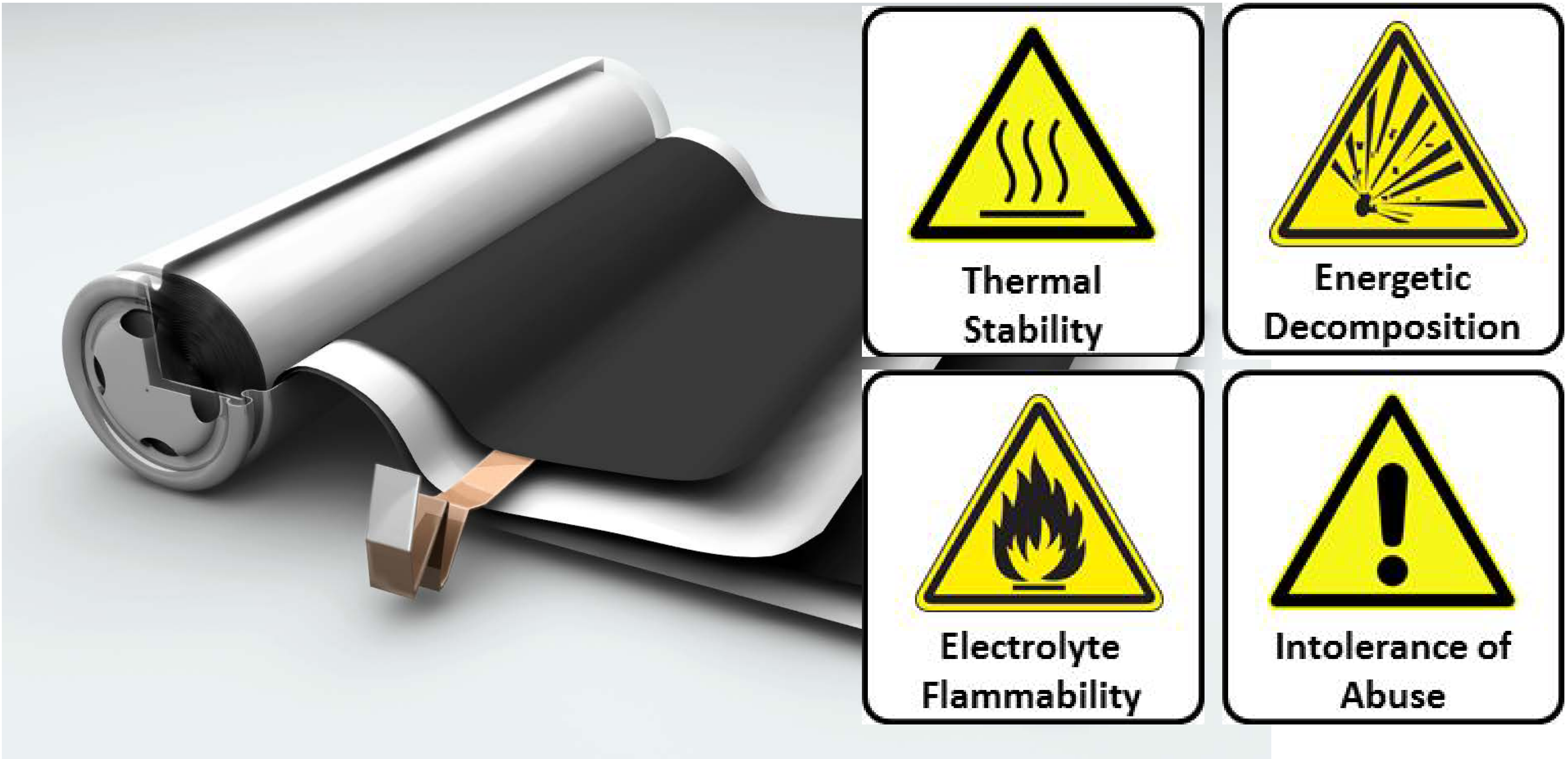
## Abuse Resilient Component Development:

- **LiF/ABA Electrolytes**
  - Abuse testing of LiF/ABA in NMC cells shows abuse response similar to COTS LFP cells
  - Scale-up of LiF/ABA at ANL MERF
  - Identification and synthesis of two new candidate ABAs
  - Evaluation of LiF/ABA from ANL shows comparable performance to small lot batch
  - Scaled-up LiF/ABA will enable a more complete evaluation of this component

## Abuse Resilient Electrolyte Evaluation:

- **LiF/ABA (SNL), Phosphazene (INL), Organosilicon (Silatronix), HFE (SNL).**
  - Initial characterization of baseline $LiPF_6$/EC:EMC, LiF/ABA, and HFE-based electrolytes is in progress
  - Results show HFE to give moderate electrochemical performance but is non-flammable during cell venting failure conditions
  - Results show LiF/ABA to mitigate the severity of thermal runaway relative to the baseline $LiPF_6$-based electrolytes

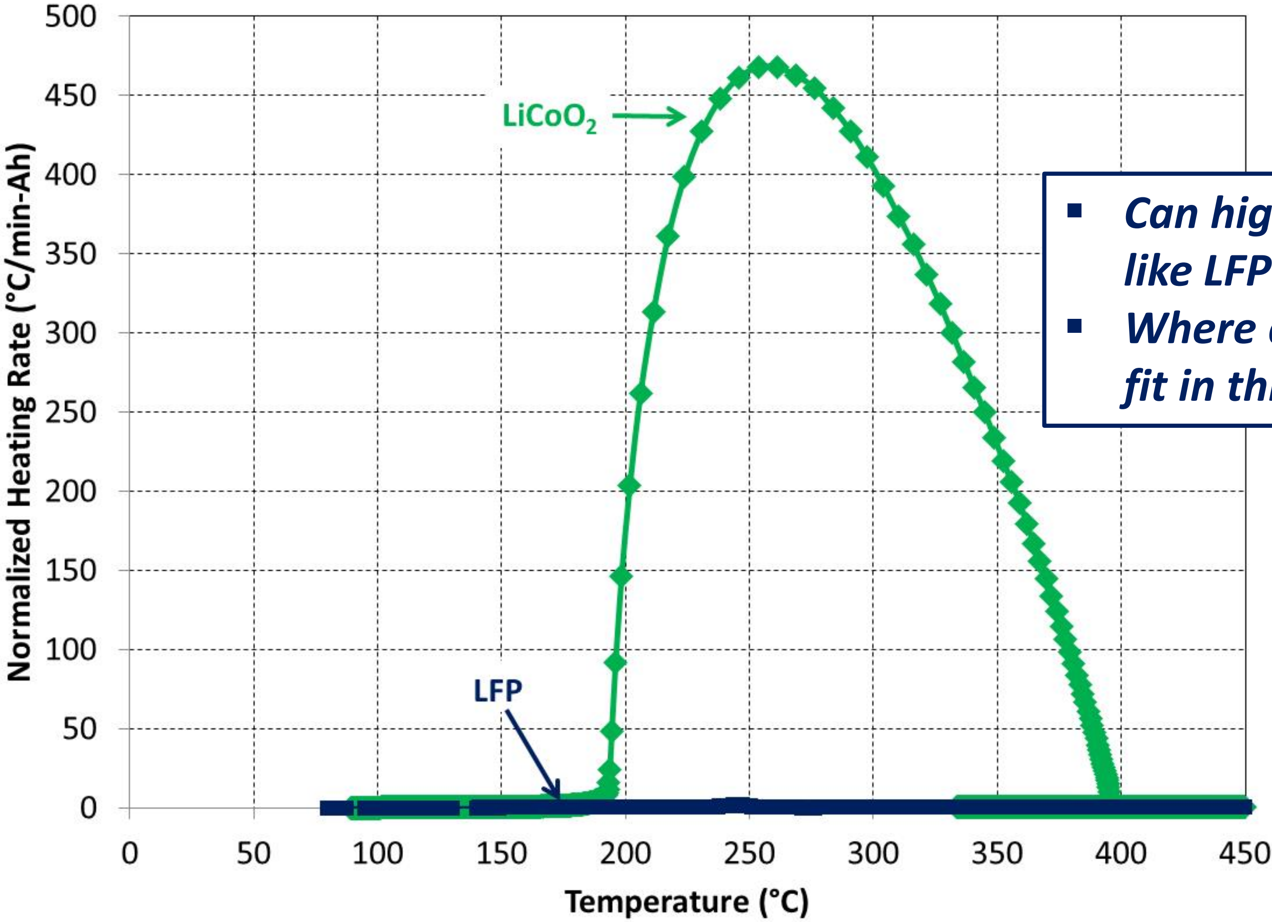
# Challenges with Inherent Cell Safety




***Need to address these issues at the cell materials level in order to field the most inherently safe energy storage products***

# Abuse Tolerance of High Energy Materials

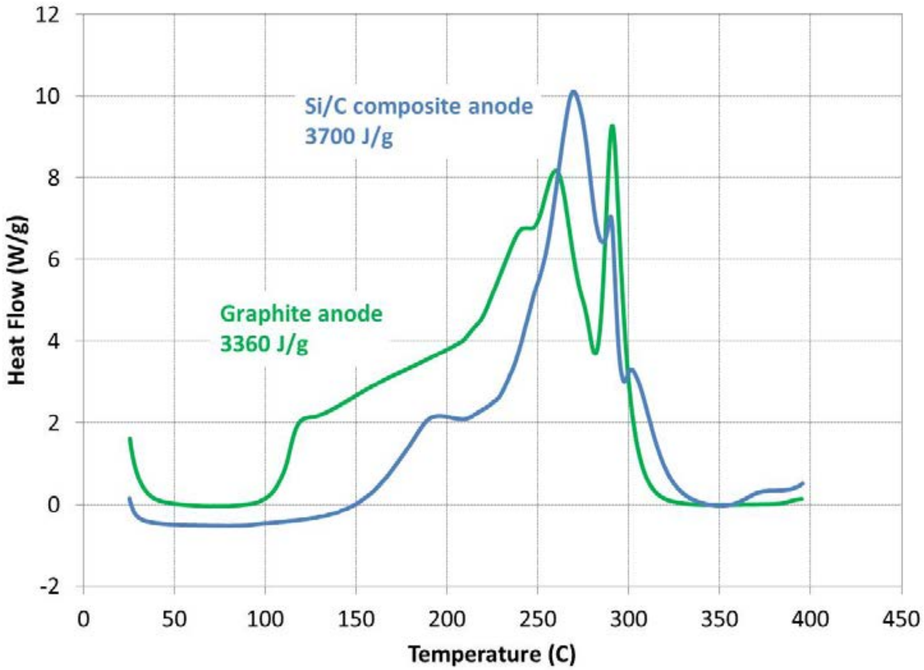
***Quantifying Thermal Runaway Energetics of Cathode Materials in Lithium-Ion Cells***




- ***Can high energy cathodes behave like LFP during thermal runaway?***
- ***Where do LMR-NMC, HV materials fit in this comparison?***

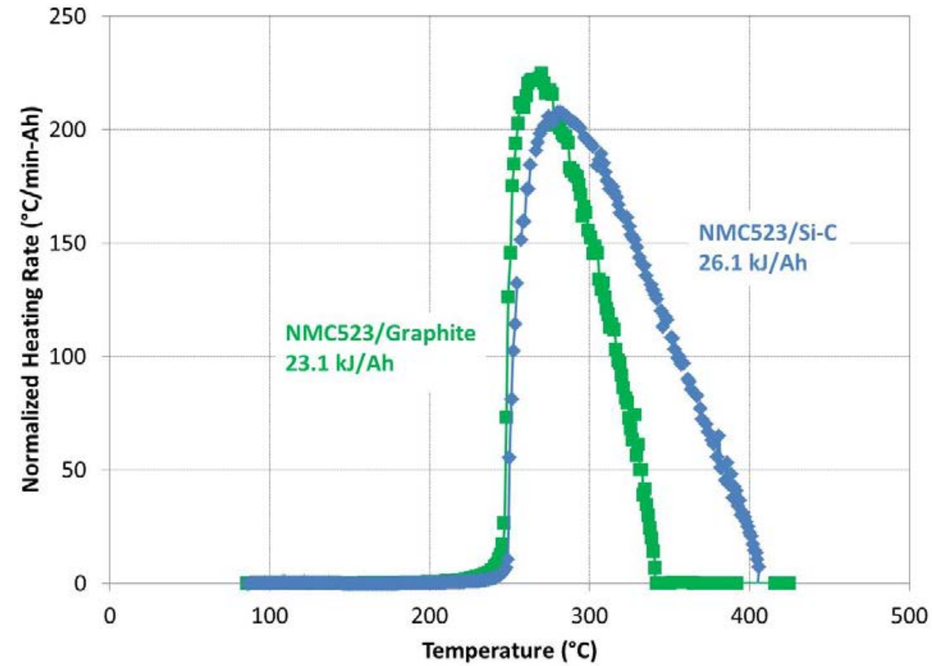
# Intermetallic Anodes

***Calorimetry on Si/C Materials***




~10% increase in heat generation over graphite

***Calorimetry on Si/C in 18650 Cells***




~10% increase in heat generation in cells

***Thermal runaway enthalpy of Si/C-NMC cells is ~10% greater than Graphite-NMC cells***

# Abuse Resilient Component Development

***LiF/ABA electrolytes designed to mitigate the severity of lithium-ion cell thermal runaway***

**Summary of Accomplishments:**

- **Demonstration of abuse tolerance (OC & TR)**
- **Delivery of LiF/ABA synthesis to ANL MERF in Q1 FY15**
- **100 g LiF/ABA scaled-up at ANL MERF in Q2 FY15**
- **40 g LiF/ABA delivered to SNL for evaluation**
- **scaled up LiF/ABA performance comparable to small batch LiF/ABA (data in following slides)**
- **Submission of high temperature LiF/ABA samples to ANL CAMP for analysis**

# Advanced Electrolyte Development

***Objective: Systematically evaluate a series of electrolytes to determine the relative electrochemical performance and abuse tolerance in NMC/graphite cells***

| Candidate Electrolytes | | |
|---|---|---|
| **Electrolyte** | **Formulation** | **Advertised Attributes** |
| Baseline | 1.2 M $LiPF_6$ in EC:EMC (3:7) | Good electrochemical performance<br>Not particularly good abuse tolerance, flammable, etc. |
| ABA | 1.0 M LIF/ABA + 2% VC | Mitigate the severity of a cell thermal runaway, enhance abuse tolerance |
| Phosphazene (FM2) | 1.2 M $LiPF_6$ in EC:EMC (3:7) + 10% FM-2 | Flame retardant, limit the severity of a cell thermal runaway |
| Organosilicon (OS) | Proprietary | Thermally Stable |
| Hydrofluoro ether (HFE) | 1.0 M LiTFSI in EC:DEC:HFE (5:45:50) | Non-flammable, minimal impact on electrochemical performance |

# Metrics for Performance

- **Performance metrics**
  - **Conductivity[1] - ≥ 12 mS/cm at RT**
  - **Voltage stability[1] – Stable to 5.0 V**
  - **Discharge capacity – 10% of baseline**
  - **Cycle life[1] – ≥80% capacity retention @ 1000 cycles (full DOD)**
- **Abuse tolerance metrics[2]**
  - **ARC – Heating rate < 5 °C/min**
  - **Thermal Ramp – EUCAR ≤4**
  - **Overcharge – EUCAR ≤4**
  - **Flammability – no ignition, no sustained fire**



**[1]DOE EV goals/USABC Electrolyte RFPI; [2]SNL developed abuse tolerance metrics**

# Advanced Electrolyte Development

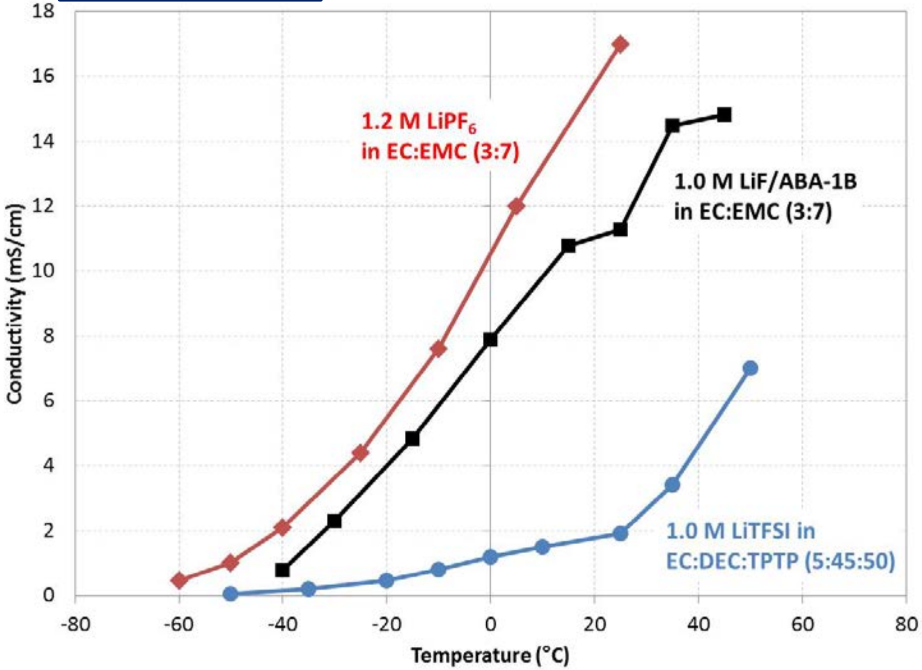
| Evaluation Matrix | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Electrolyte | Performance | | | | | Abuse Tolerance | | | | |
| | Conductivity | CV | Capacity | Cycle life | Rate | DSC | ARC | Thermal | Overcharge | Flammability |
| **Baseline** | | | | | | | | | | |
| **ABA** | | | | | | | | | | |
| **FM2** | | | | | | | | | | |
| **OS** | | | | | | | | | | |
| **HFE** | | | | | | | | | | |

**Complete**

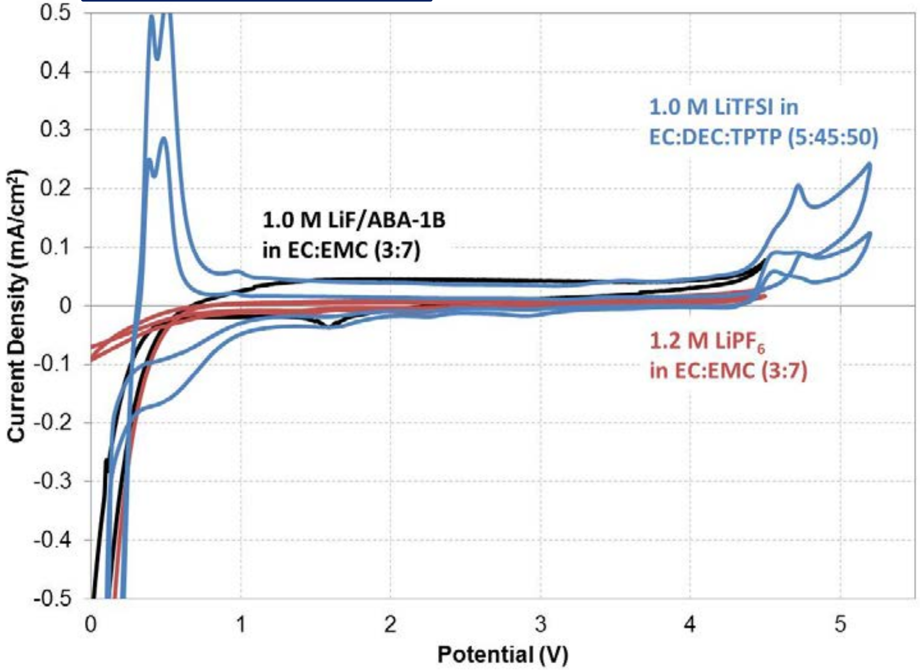
**In progress**

# Electrochemical Performance

***Conductivity***



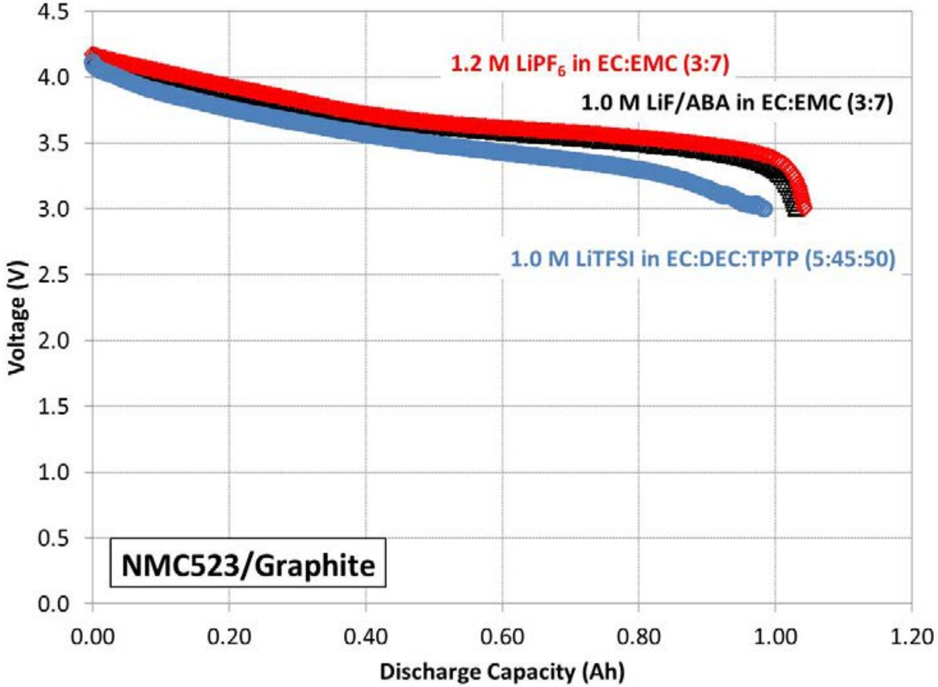

***Cyclic Voltametry***



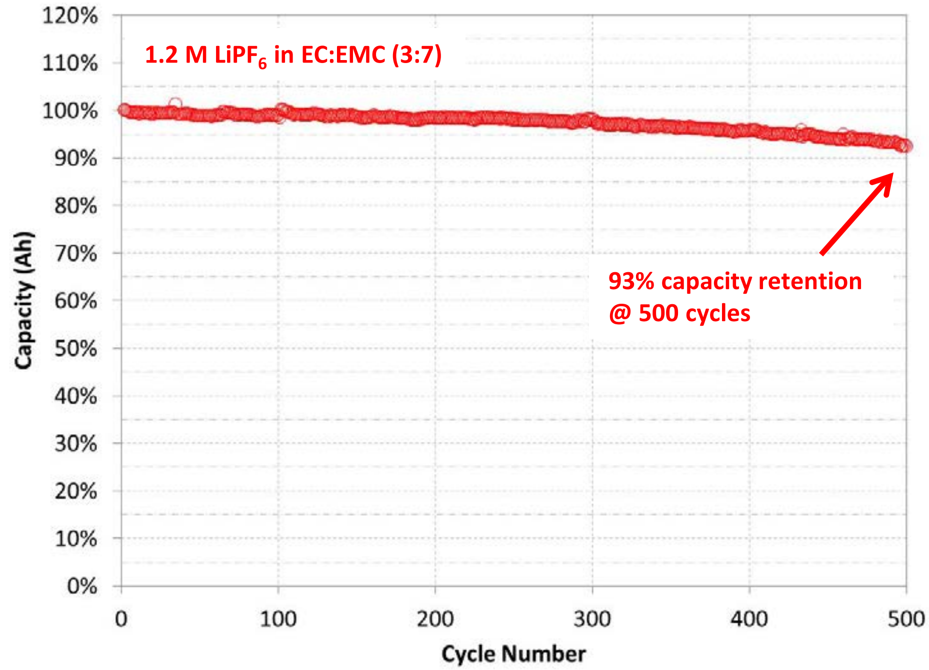

***LiF/ABA conductivity > 10 mS/cm, HFE conductivity significantly less***
***< 50 µA/cm$^2$ for HFE and < 75 µA/cm$^2$ for LiF/ABA at 4.5V***

# Electrochemical Performance

**_Discharge Capacity_**



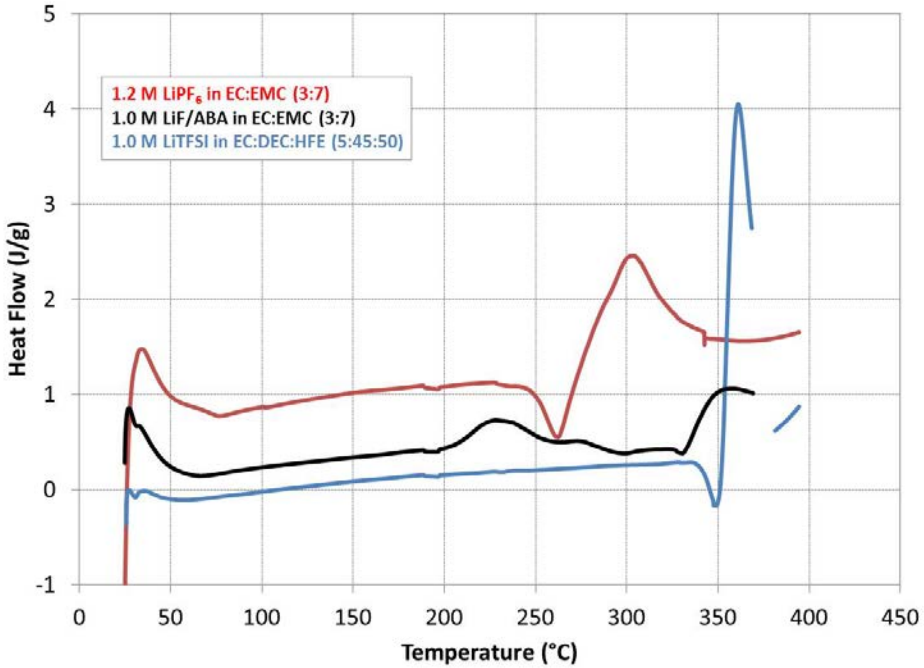

**_Cycle Life_**



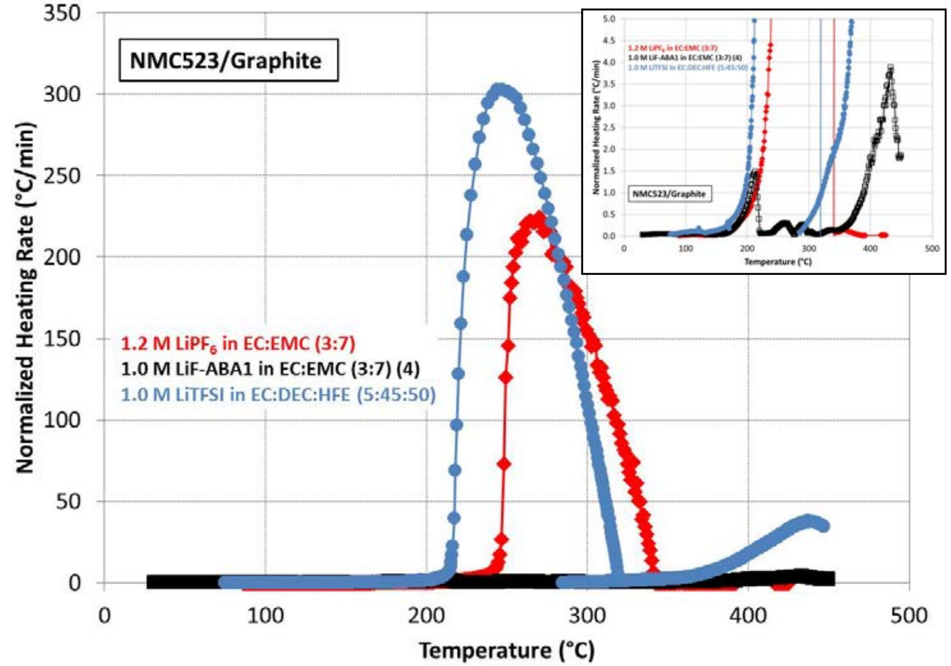

***5th cycle discharge capacity LiF/ABA comparable to baseline; HFE cell ~5% less capacity***
***Baseline gives 93% capacity retention at 500 cycles (no additives)***

# Abuse Tolerance

**Differential Scanning Calorimetry (DSC)**



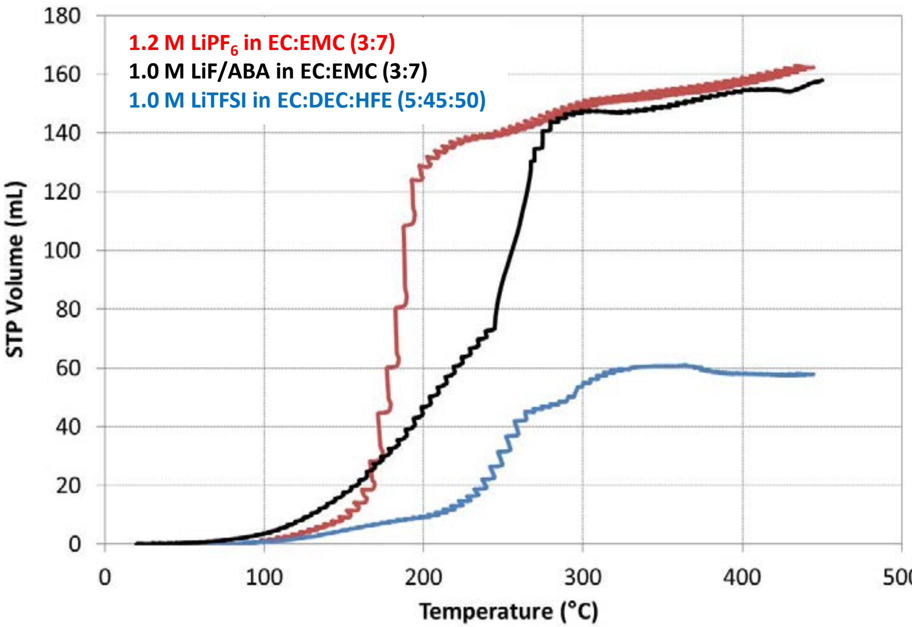

**Accelerating Rate Calorimetry (ARC)**



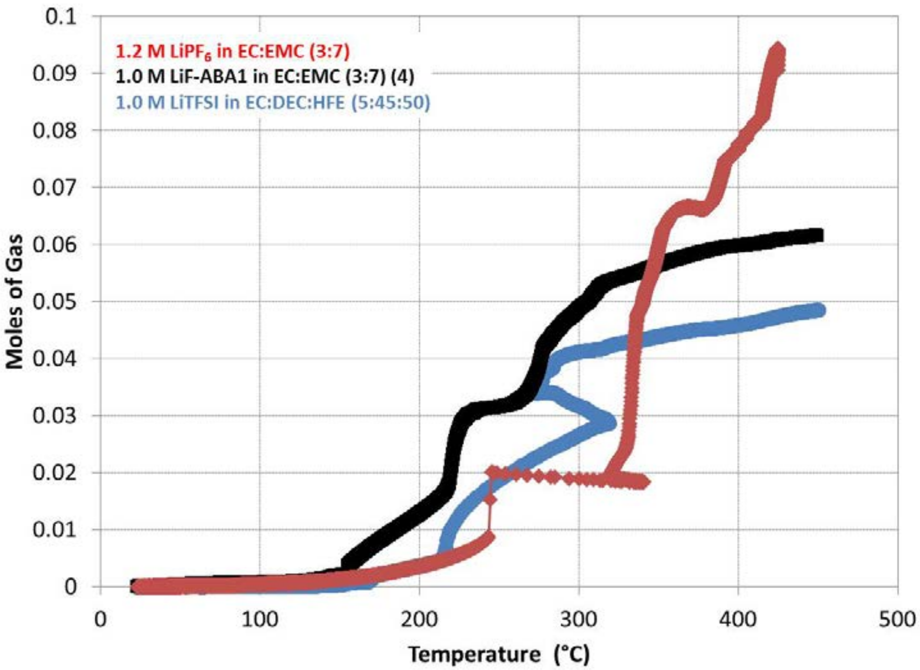

- ***Significant reduction in the thermal runaway free energy of NMC cells with LiF/ABA electrolytes***
- ***Higher thermal runaway free energy of NMC cells with HFE electrolytes likely due to the DEC solvent component (*****$\Delta H_c$ (DEC) = 2715 kJ/mole, $\Delta H_c$ (EMC) ~ 2000 kJ/mole)**

# Electrolyte Gas Generation

***Electrolyte ARC bomb gas volume***




***Cell ARC gas volume***




***~60% reduction in gas volume between baseline and HFE electrolyte***
***~40% reduction in gas volume at the cell-level between baseline and HFE electrolyte***
***~30% reduction in gas volume at the cell-level between baseline and LiF/ABA electrolyte***

# Abuse Tolerance

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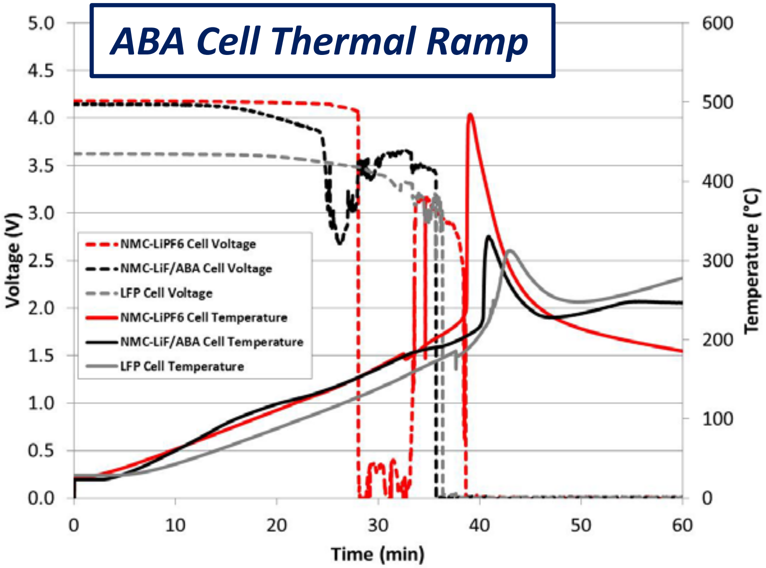
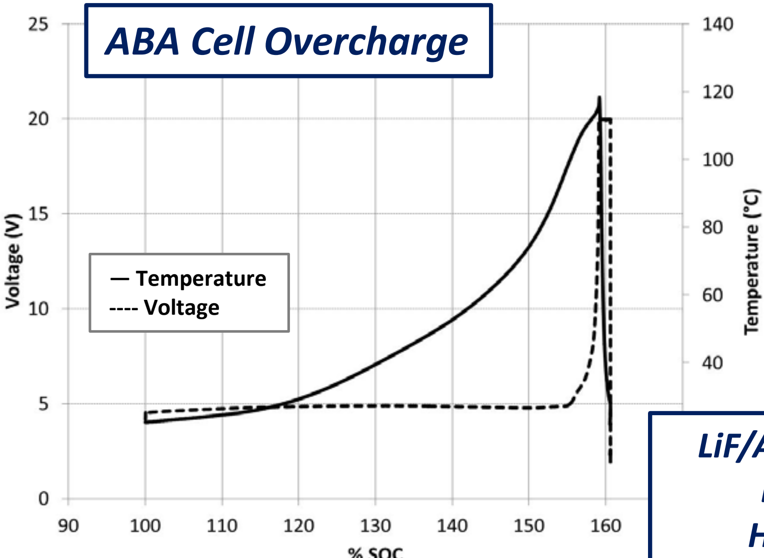
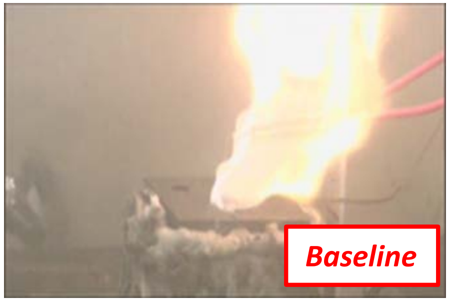
## ABA Cell Thermal Ramp



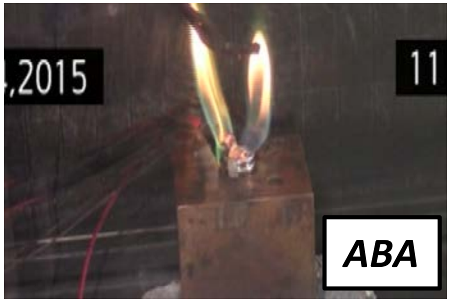

## ABA Cell Overcharge




## Cell Vent Flammability Measurements








***LiF/ABA cells are more abuse tolerance than their baseline counterparts***
***LiF/ABA in carbonate solvents is flammable in a cell vent failure***
***HFE electrolyte at 50% HFE is non-flammable in a cell vent failure***

# Collaboration and Coordination with Other Institutions

- **HE Materials**
  - XG Sciences
  - ANL
  - NEI
- **Abuse Resilient Component Development**
  - Binrad Industries
  - ANL MERF
  - ANL CAMP
- **Electrolyte Evaluation**
  - INL
  - Silatronix
  - ANL (MERF)

# Proposed Future Work

- Complete evaluation of intermetallic anode materials (runaway response, abuse tolerance, gas generation)
- Evaluation of abuse tolerance of materials developed from the competitive ABR projects
- Evaluation of new candidate LiF/ABA electrolytes with enhanced performance and abuse tolerance characteristics
- Completion of the electrolyte evaluation study and recommendation to DOE of the most promising abuse tolerant electrolyte materials for follow-on work
- Support the safety related elements of the of DOE EBMR, ABR, Testing, CAEBAT, and USABC programs

# Summary

- Fielding the most inherently safe chemistries and designs can help address the challenges in fielding large-scale lithium-ion
- Materials choices can be made to improve the inherent safety of lithium-ion cells
- LiF/ABA electrolytes show comparable electrochemical performance to $LiPF_6$/carbonate baseline electrolyte and cells and cycle life evaluation is currently in progress
- LiF/ABA electrolytes show a significant improvement in thermal runaway response and abuse tolerance of NMC cells; almost eliminating the high rate runaway reaction in some cases
- HFE electrolyte shows modest electrochemical performance compared to $LiPF_6$/carbonate baseline electrolyte with reduced conductivity, good high voltage stability, and ~5% loss in discharge capacity in NMC cells
- HFE electrolytes show a significant reduction in the total gas generation and no ignition or flammability under a cell vent failure; thermal runaway performance is more energetic in the HFE electrolyte, but that is likely due to the DEC component
- Evaluation of organosilicon and phosphazene electrolytes are in progress

# Acknowledgements

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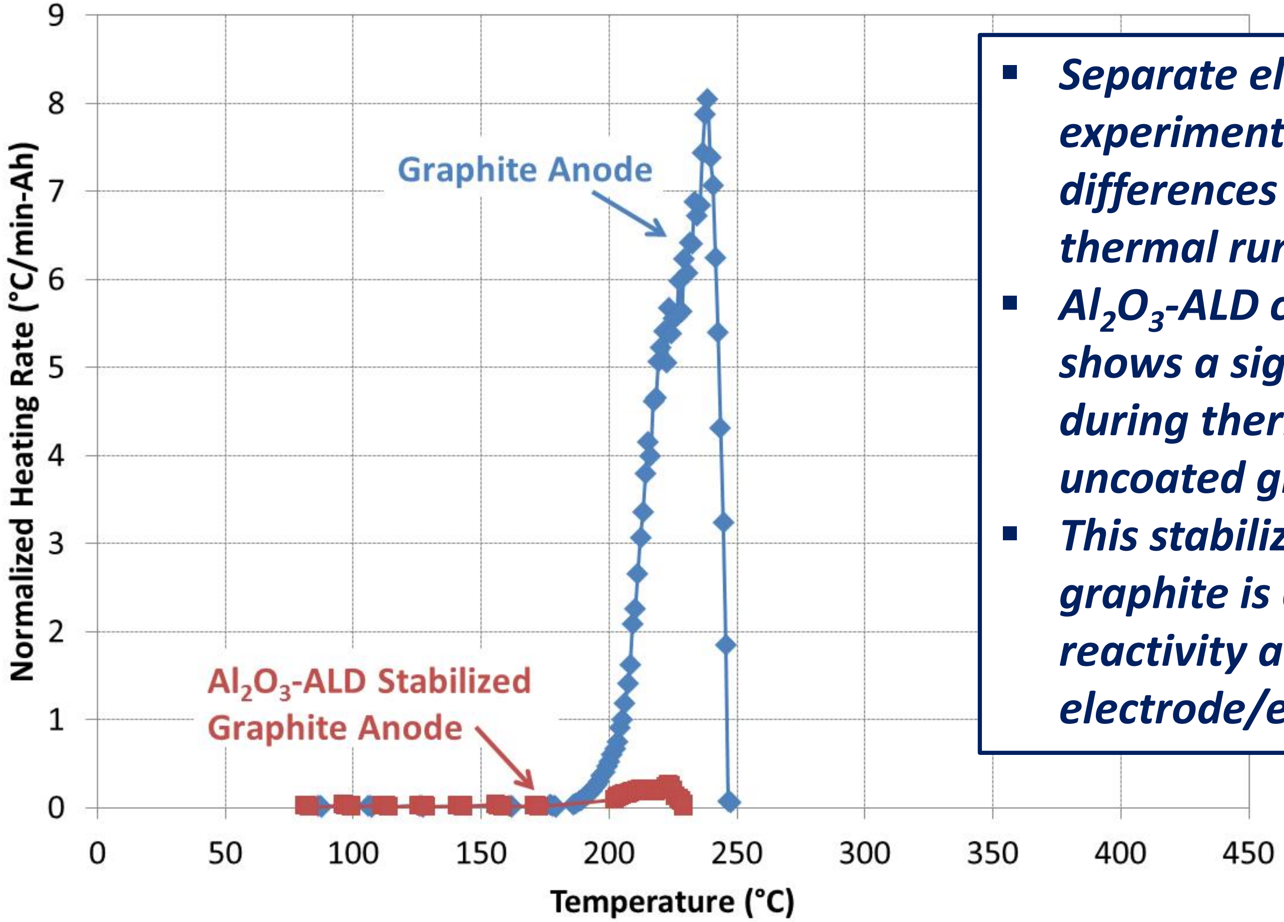
- Lorie Davis
- Scott Spangler

# TECHNICAL BACK-UP SLIDES

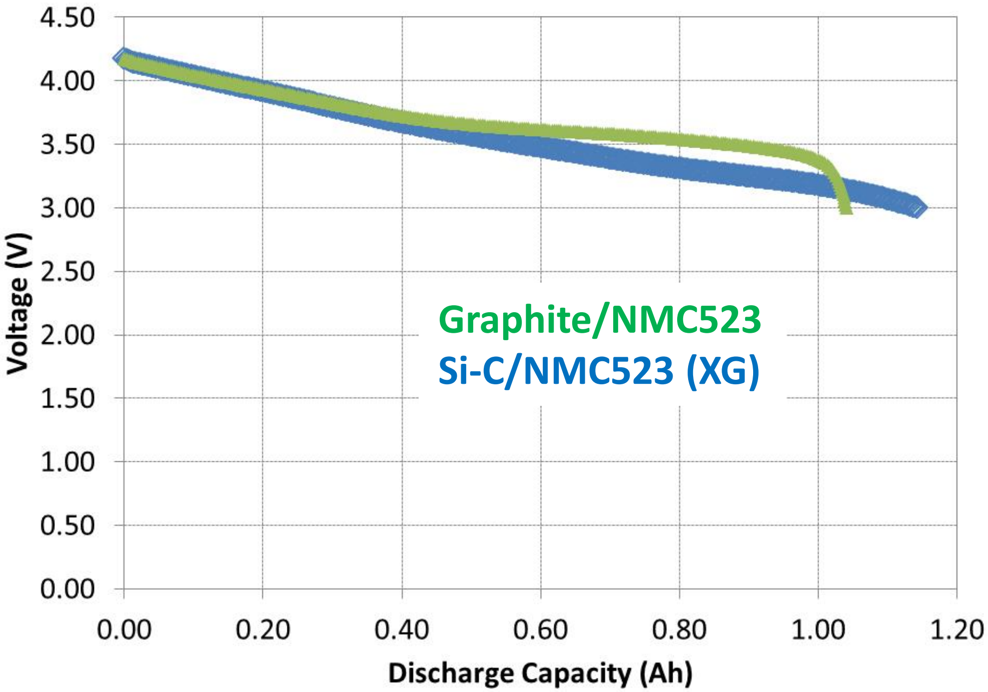
# Abuse Tolerance of Active Materials

***Quantifying Thermal Runaway Energetics of Anode Materials in Lithium-Ion Cells (Collaboration with CU-Boulder)***




- ***Separate electrode ARC experiments are used to quantify differences in active material thermal runaway***
- ***$Al_2O_3$-ALD coated graphite does shows a significant stabilization during thermal runaway relative to uncoated graphite electrodes***
- ***This stabilization of the $Al_2O_3$-ALD graphite is attributed to diminished reactivity at the electrode/electrolyte interface***

# Abuse Tolerance of Intermetallic Anodes

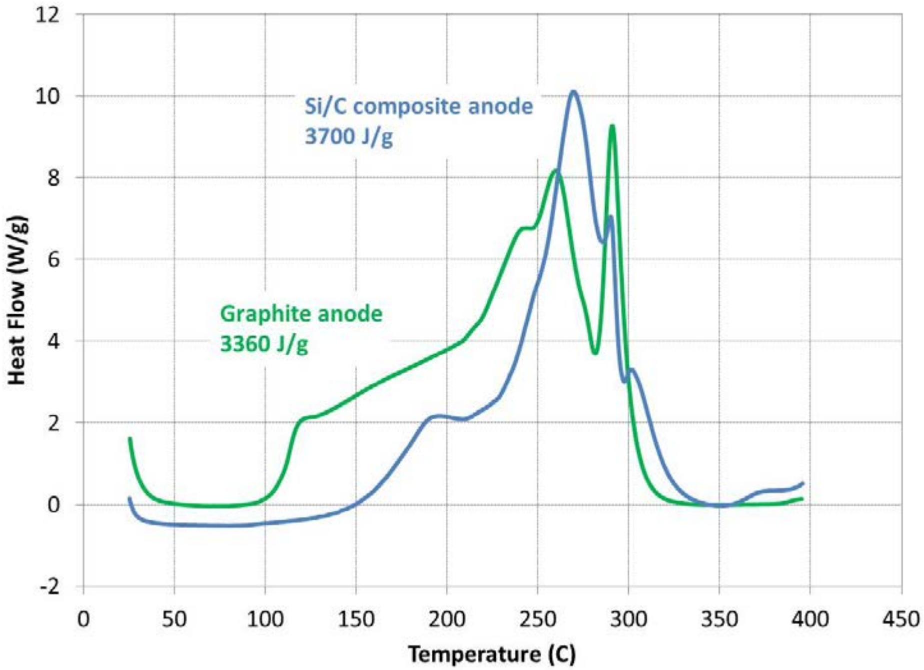



***Key Questions:***

- ***General impact of intermetallic anodes on thermal runaway response (heat release)?***
- ***Impact of intermetallic anodes on electrolyte reactivity, decomposition, & gas generation?***
- ***Abuse response of intermetallic anodes (any unanticipated failure modes or intolerance to abuse conditions relative to graphite)?***
- ***Support development efforts to improve loading, cycle life and power over time***

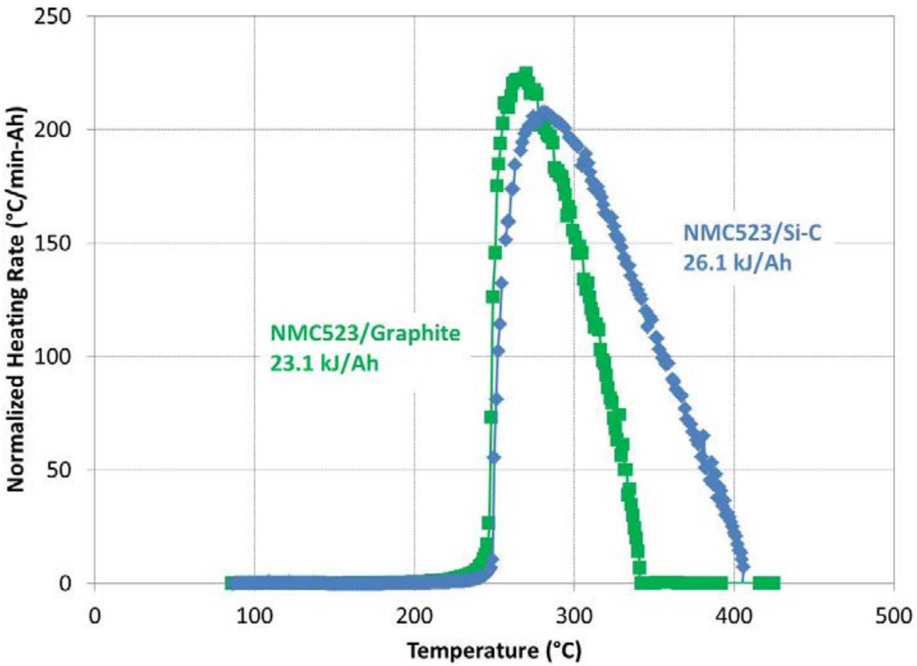
# Intermetallic Anodes

***Calorimetry on Si/C Materials***




***~10% increase in heat generation over graphite***

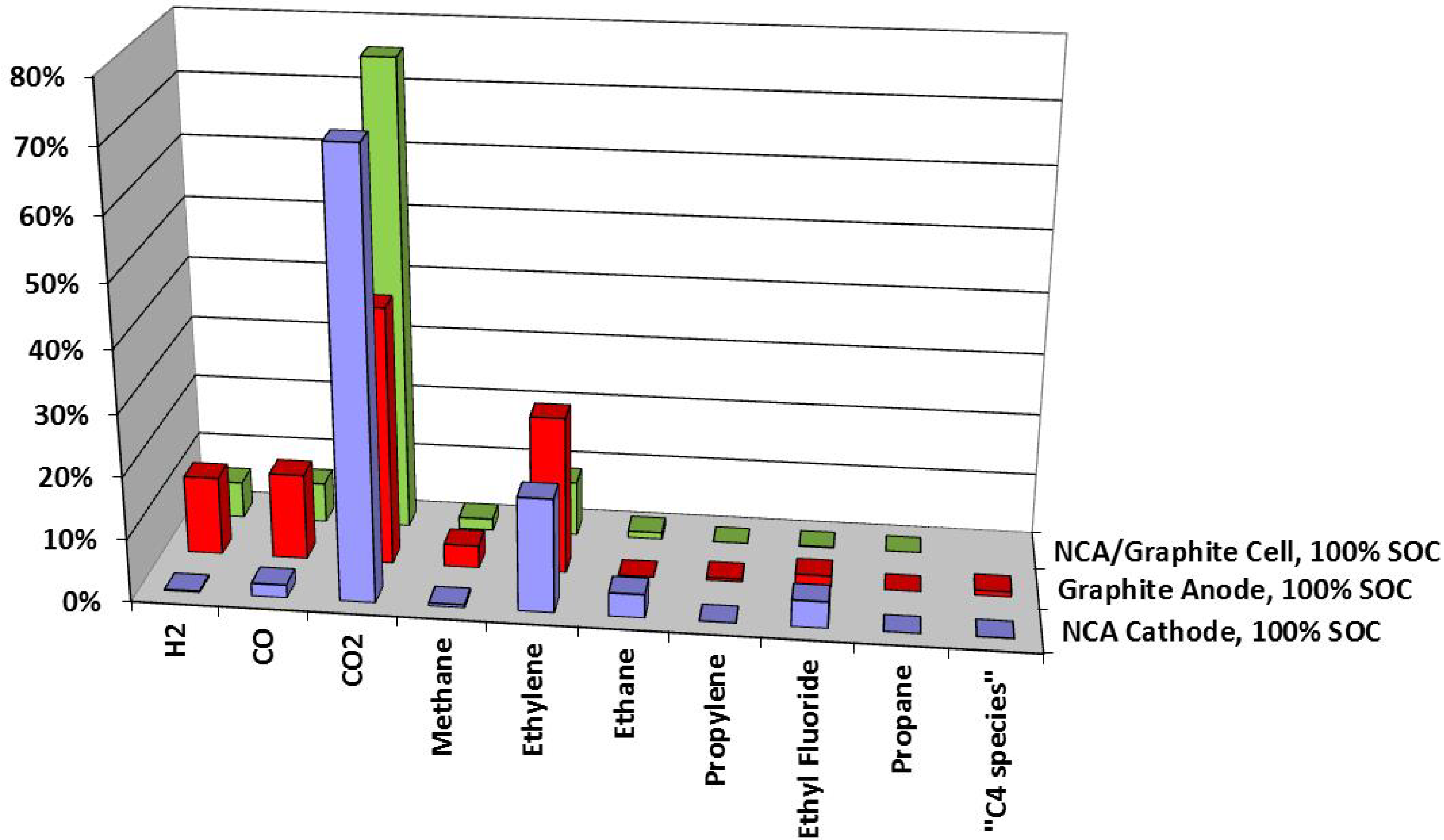
***Calorimetry on Si/C in 18650 Cells***




***~10% increase in heat generation in cells***

***Thermal runaway enthalpy of Si/C-NMC cells is ~10% greater than Graphite-NMC cells***

# Vent Gas Analysis from the ARC




***18650 cell electrodes separated from a cell at 100% SOC and repackaged in 18650 cans***
***Grab samples collected during an ARC experiment and analyzed***
***Analysis show significantly more $H_2$ and CO generation at the anode interface***

# Abuse Tolerance of Intermetallic Anodes

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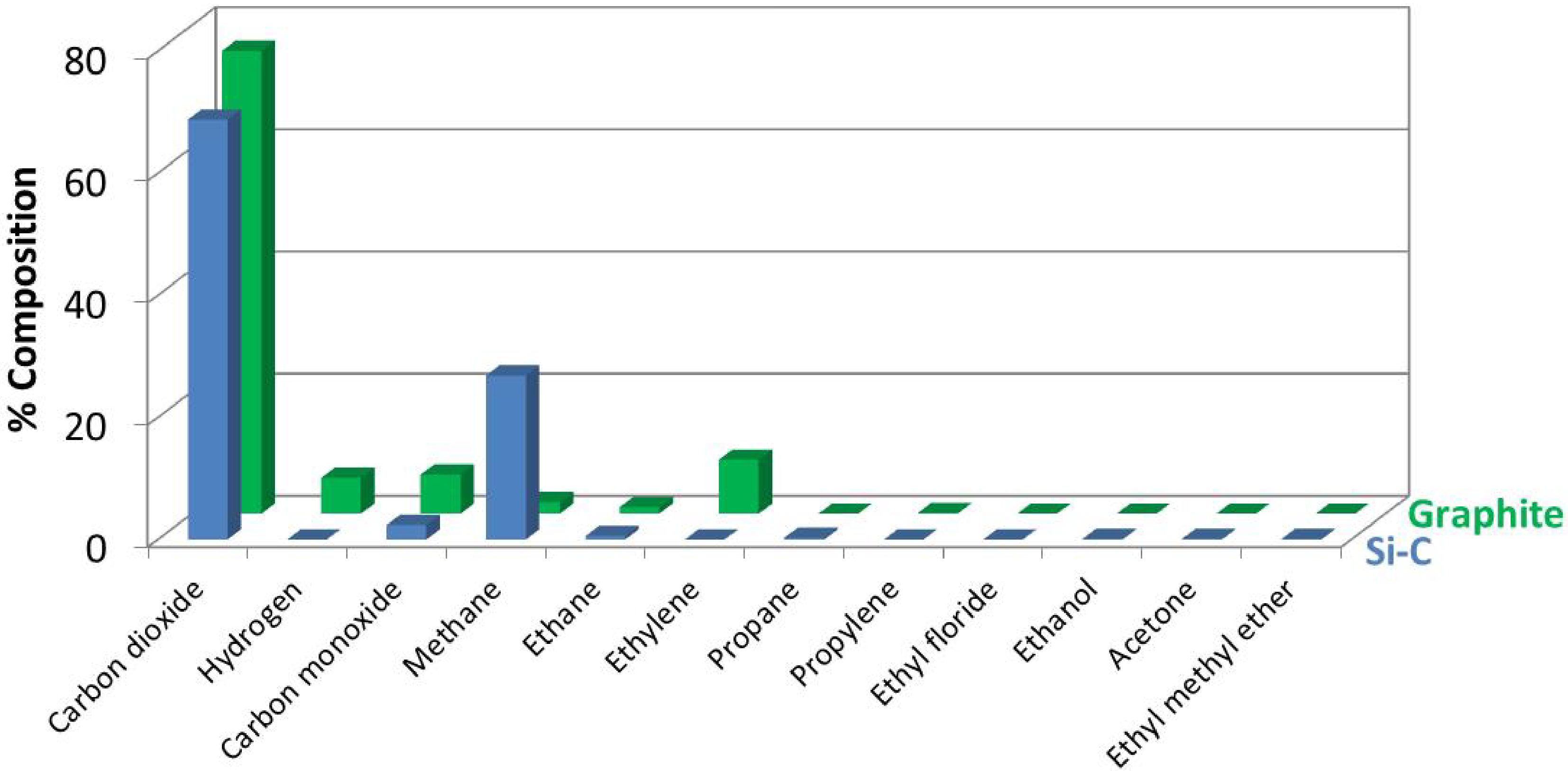
***Quantifying Gas Generation from Anode Materials in Lithium-Ion Cells***




***No experimental or DFT/simulation work on electrolytes + Si to study gas generation***
***Engage PTF for electrode analysis to elucidate the reaction mechanism of electrolyte + Si***